# On the Relative Stabilities of Singlet and Triplet Oxyallyl and Cyclopropanone: A Density Functional Study

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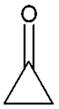
**Keywords:** Density-functional theory / Oxyallyl / Cyclopropanone / ab initio Calculations / Radicals

Density functional calculations (B3LYP/6–31G*) have been carried out for cyclopropanone and the singlet and triplet electronic states of oxyallyl, as well as for several bicyclic systems that incorporate the cyclopropanone ring. The results of these calculations, when compared to those obtained with more sophisticated multi-determinant calculations performed previously, agree both qualitatively and quantitatively.

## Introduction

Over the past several years there has been intense interest in experimental[1−8] and theoretical[9−16] investigations of the role of oxyallyl (**1**) in the ring opening reactions of cyclopropanone (**2**) and allene oxide. Problems that have been addressed in these studies range from the stereochemistry of the ring opening of cyclopropanones to the identification of the electronic ground state of oxyallyl.



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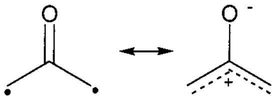
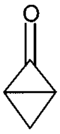


**1**

The present investigation was prompted by a very extensive and systematic study[15] of the neutral $C_3H_4O$ potential surface based on the results of multi-determinant calculations. Recently we have performed[16] a theoretical investigation of the $C_3H_4O$ potential surface, focused on the conversion of allene oxide to cyclopropanone, and the ring opening reactions of cyclopropanone, both of which involve oxyallyl as an intermediate. The density functional theory (B3LYP/6−31G*) and complete active space SCF (CASSCF) techniques with inclusion of dynamic correlation taking into account Roos′ method (CASPT2N) [17−21] were employed. It was found that the B3LYP/6−31G* results were essentially identical to those obtained with CASSCF/CASPT2N. Since B3LYP/6−31G* is a single determinant method, while CASSCF is based on a multideterminant wavefunction, the very good agreement between these two approaches seems surprising. However, the results of other investigations[22−30] support our conclusions about the precision of the B3LYP/6−31G* results in relation to those obtained with much more elaborate and extended theories. Houk has also concluded that the B3LYP/6−31G* method "is remarkably robust" for the study of reactions that involve diradical pathways.[31]

Our analysis considered the relationship between singlet oxyallyl, allene oxide and cyclopropanone. It would also be interesting, however, to compare the B3LYP/6−31G* results for triplet oxyallyl with those obtained from more advanced methods. Such investigations would also provide an answer to the question of whether the B3LYP/6−31G* method might be an appropriate method to study both the singlet and triplet surfaces of oxyallyl. We note that the authors of ref.[15] concluded that B3LYP/6−31G* is not appropriate for singlet oxyallyl, while our results[16] contradict this opinion. To further support our conclusions we also considered the very interesting bicyclic systems **3** and **4** in which a cyclopropanone ring is incorporated into a bicyclic structure.



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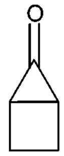

**4**

Previous results have shown that the behavior of these two systems is very different (ring openings) from that of cyclopropanone. All systems studied here provide a challenge for theory since they involve not only highly strained rings, but also open shells in the oxyallyls that are notoriously difficult to describe theoretically.

## Results and Discussion

### Cyclopropanone

In the theoretical study of the ring opening of allene oxide to oxyallyl,[16] it was found that singlet oxyallyl is formed as an intermediate on the potential surface with both the B3LYP/6−31G* and CASSCF methods, and that it was predicted to be about 30 kcal/mol higher in energy than its closed form, cyclopropanone (see Table 1). The

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transition structure linking oxallyl with cyclopropanone was also located. As mentioned above the authors of ref.[15] stated that the B3LYP/6−31G* method does not accurately describe the singlet state of oxyallyl. However, this conclusion was based on results obtained with RHF B3LYP/6−31G* and, as we have recently shown,[16] this method leads to an "unstable" wavefunction for singlet oxyallyl. In order to properly describe the singlet state of oxyallyl the UHF B3LYP/6−31G* method must be used, which does give excellent agreement with the results of the more advanced multi-determinate methods.[35] Furthermore, while the unstable RHF B3LYP/6−31G* solution is found to be a transition structure, the results of UHF B3LYP/6−31G* show it to be a minimum on the potential surface as was predicted by the reliable multi-determinant methods. We note here that a broken-spin-symmetry wavefunction was obtained for the UHF B3LYP/6−31G* calculation of singlet oxyallyl ($S^2 = 0.836$) as was also the case for the other singlet diradicals discussed below (see Table 1).[36]

Table 1. B3LYP/6−31G* energies in a.u.; zero point energies and energies relative to the singlet and triplet oxallyls of the corresponding cyclopropanone (including ZPE corrections) in kcal/mol

| Molecule | energy | $S^2$ | ZPE | $E^{\circ}_{\mathrm{rel.}}$ |
|---|---|---|---|---|
| **2** | −191.88074 | – | 38.4 | 0 |
| **1s** | −191.83339 | 0.836 | 36.1 | 27.4 |
| **1t** | −191.83568 | – | 36.1 | 26.0 |
| **3** | −229.95805 | – | 42.8 | 0 |
| **5s** | −229.91483 | 0.693 | 40.7 | 25.0 |
| **5t** | −229.90890 | – | 39.9 | 27.9 |
| **4** | −269.27036 | – | 61.1 | 0 |
| **6s** | −269.27491 | 0.623 | 59.7 | −4.3 |
| **6t** | −269.26542 | – | 59.1 | 1.1 |
| **7** | −386.00885 | – | 101.8 | 0 |
| **8s** | −386.00654 | 0.665 | 100.7 | 0.3 |
| **8t** | −385.99947[a] | – | 100.2 | −4.3 |

[a] Ref.[8]

In light of the fact that B3LYP/6−31G*, when properly applied, yields a good result for singlet oxyallyl, the question arises as to whether B3LYP/6−31G* would perform equally well for oxyallyl in the triplet state. Previous multi-determinant calculations have predicted that the singlet and triplet forms of oxyallyl lie very close in energy to each other (0.1−1.4 kcal/mol), with the triplet always predicted to be lower in energy.[9][15] Indeed UHF B3LYP/6−31G* [32][33] also makes the same prediction, with the singlet placed only 1.4 kcal/mol above the triplet (see Figure 1).

Hence it appears that B3LYP/6−31G*, in addition to giving the same qualitative picture of the relationship between cyclopropanone, singlet oxyallyl and triplet oxyallyl, also gives essentially the same quantitative picture. There is also good agreement in the geometries of the structures **1s** and **1t** calculated by B3LYP/6−31G* and CASSCF (see Figure 2).

## Bicyclo[1.1.0]butanone

Bicyclo[1.1.0]butanone (**3**) has proved to be a very interesting example of the cyclopropanone-oxyallyl system. The cyclopropanone is fused into a bicyclic system that contains two highly strained three-membered rings in which the cen-

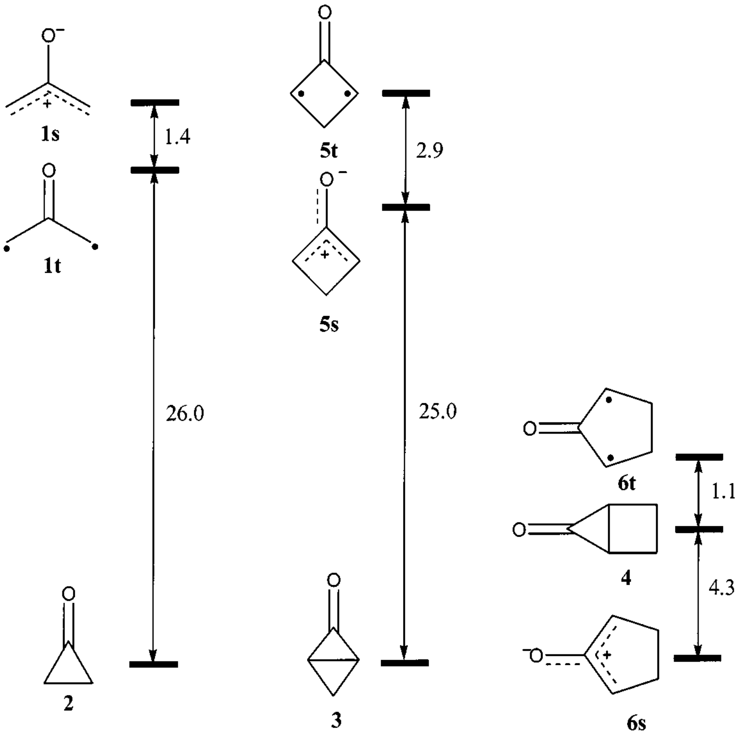
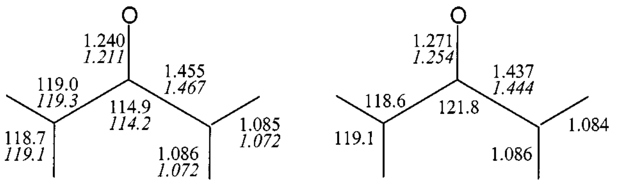


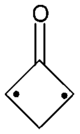
Figure 1. Relative energies in kcal/mol of the cyclopropanones and their open singlet and triplet forms; no comparison of absolute energies between the three systems is implied



**1s** **1t**

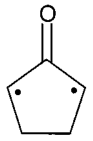
Figure 2. B3LYP/6−31G* and CASSCF (in italics) geometries of singlet and triplet oxyallyl; CASSCF geometries for **1s** are from ref.[14] and for **1t** from ref.[9]; angles are in degrees and bond lengths in angstroms

tral bond, if broken, would yield an oxyallyl (**5**) with a considerable portion of the strain in the bicyclic system relieved.



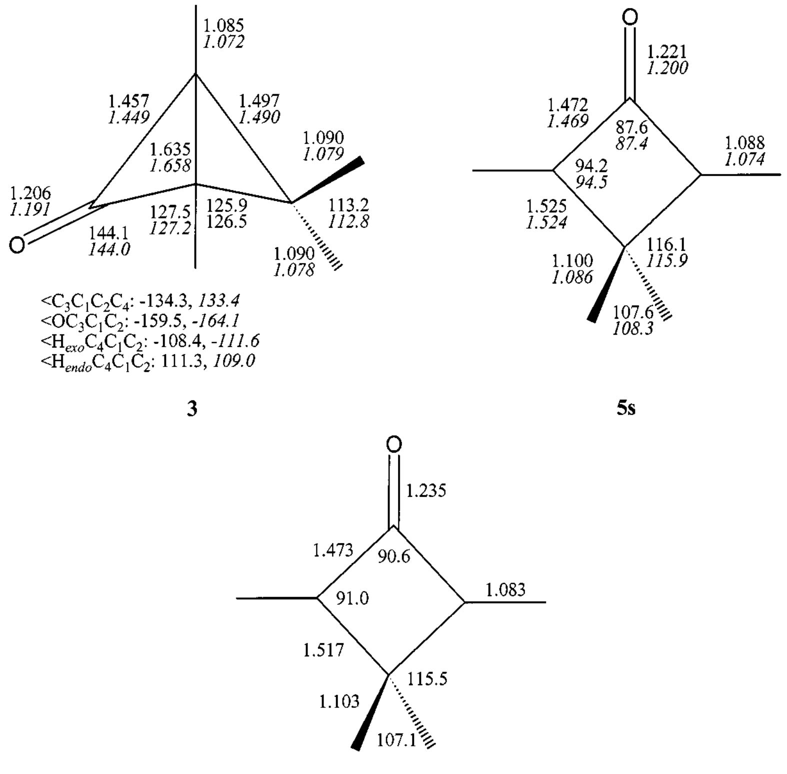
**5**

It was first reported in 1990[13] in a CI study that singlet oxyallyl (**5s**) is predicted to be more stable by 3.7 kcal/mol than the triplet (**5t**), just the opposite of what was found for the singlet and triplet states of the parent oxyallyl. It has been argued that the substitution of a carbon atom for two of the hydrogens in oxyallyl might stabilize the singlet



**6**

state (**5s**) (contribution from the zwitterionic resonance structure) to a greater extent than the triplet state (**5t**). However, the singlet (**5s**) was still found to lie 34 kcal/mol higher in energy than bicyclo[1.1.0]butanone. Subsequently Borden studied this system[4] and, with the CASPT2N method, found that **5s** lies 27.6 kcal/mol higher in energy than **3**. Furthermore **5s** was found to be a transition structure which presumably links in a degenerate reaction the two bent forms of bicyclo[1.1.0]butanone. We performed B3LYP/6−31G* calculations (Table 1) on **3, 5s** and **5t** and again found the results to be very close to those previously obtained by Borden. The singlet **5s** (a transition structure) was found to be 2.9 kcal/mol more stable than the triplet **5t**, and to lie 25.0 kcal/mol above its bicyclic form (see Figure 1). Both values (2.9 vs. 1.7 kcal/mol obtained with CI;[13] 25.0 vs. 27.6 kcal/mol obtained with CASPT2N[4]) are in very good agreement with those mentioned above. The B3LYP/6−31G* method also predicts **3s** to be a transition structure although, interestingly, the UHF/6−31G* calculation predicts it to be a minimum. In addition B3LYP/6−31G* computed geometries are in close agree-



**3** **5s** **5t**

Figure 3. B3LYP/6−31G* and CASSCF (in italics) geometries of cyclopropanone **3** and its singlet and triplet open forms, **5s** and **5t**; CASSCF geometries are from ref.[4]; angles are in degrees and bond lengths in angstroms

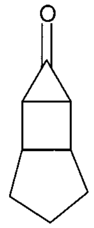
ment with those obtained with the CASSCF method as shown in Figure 3. Again B3LYP/6−31G* provides what appears to be the correct qualitative as well as quantitative picture of the relative energies and structures of **3**, **5s** and **5t**.

## Bicyclo[2.1.0]pentan-5-one

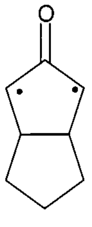
This system is a very unusual one in that bicyclo[2.1.0]-pentan-5-one (**4**) is predicted to be unstable relative to its open, singlet oxallylic form (**6s**). Lahti and co-workers first reported this to be the case in 1990,[13] having found with CI calculations that **4** lies about 3 kcal/mol above the singlet oxyallyl **6s**.

This was subsequently confirmed by Powell and Borden in 1995[11] when they reported that the results of a CASSCF/CASPT2N calculation also predict the open singlet to lie 2.7 kcal/mol below bicyclo[2.1.0]pentan-5-one (**4**). Furthermore Lahti found that the singlet oxallyl **6s** is 5.8 kcal/mol lower in energy than the triplet oxallyl **6t**, as was the case for **5s** and **5t**. The B3LYP/6−31G* results (Table 1, Figure 1) are again in excellent agreement with these calculations and they predict the same ordering for the stabilities of **4**, **6s** and **6t**. The singlet oxyallyl is predicted by B3LYP/6−31G* to lie 4.3 kcal/mol below the closed form **4** and 5.4 kcal/mol below the triplet oxyallyl **6t** (see Figure 1). B3LYP/6−31G* structures also agree well with those established by more precise calculations (Figure 4).

Very recently Matlin and co-workers[8] have described an experimental and computational study on a related system in which an additional ring is fused to the bicyclo[1.1.0]-pentan-5-one system to form the tricyclic ketone **7**. The corresponding open form **8** was generated photochemically from cycloocta-2,6-dieneone and was chemically trapped.

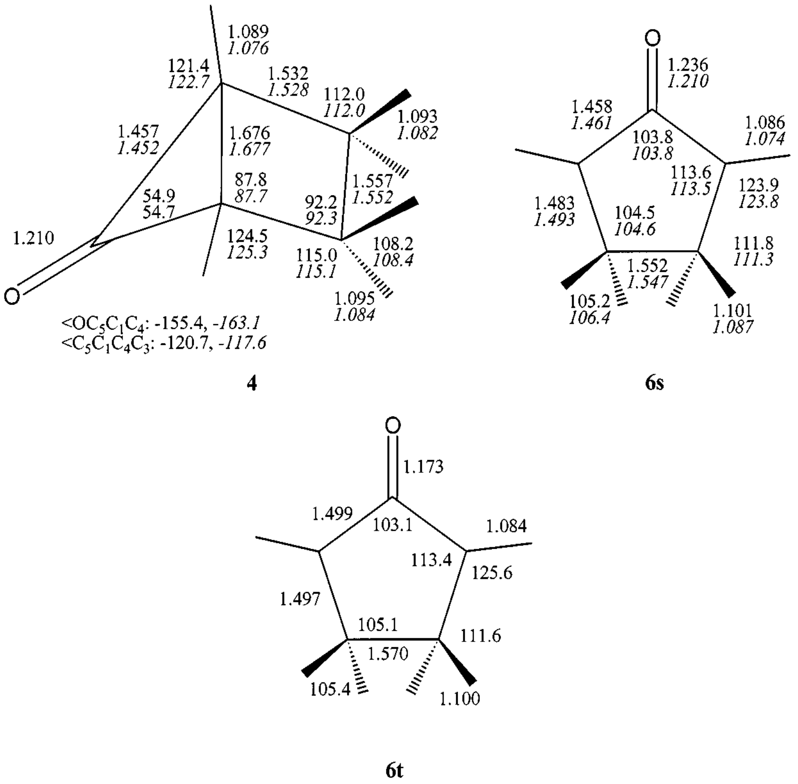


**7**



**8**

The authors also performed calculations on **8s** and **8t**, applying incorrectly the RHF B3LYP/6−31G* method for **8s**. We have repeated the calculations with UHF B3LYP/6−31G* as well as for **7** (with the rings *trans*). As in the case of the parent bicyclic[2.1.0] system it was found that **7** lies above its open singlet form **8s**. The energy separation in this case is only 0.3 kcal/mol, while **8t** is placed 4.3 kcal/mol above **8s**. Thus, given the predicted, very similar energies of **7** and **8s**, it is not surprising that they were able trap the open bicyclic form which is likely to be in equilibrium with the tricyclic ketone **7**.



**4**

**6s**

**6t**

Figure 4. B3LYP/6−31G* and CASSCF (in italics) geometries of cyclopropanone **4** and its singlet and triplet open forms, **6s** and **6t**; CASSCF geometries are from ref.[4]; angles are in degrees and bond lengths in angstroms

## Conclusions

Three very different oxyallyl systems have been studied, along with their closed-form cyclopropanones, with B3LYP/6−31G*. It was consistently found that the B3LYP/6−31G* results are in good qualitative and quantitative agreement with the predictions of calculations based on multi-determinant methods. This is the first study of these three systems that has been carried out with the same method for all structures. Due to this the results of the present analysis give some consistency to the overall picture of the oxallyl problem. Our results provide further support to the growing evidence[22−31,37−39] that B3LYP/6−31G* can be used as a reliable tool for the theoretical description of unusual organic systems, including those characterized by open shells.

## Acknowledgments

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